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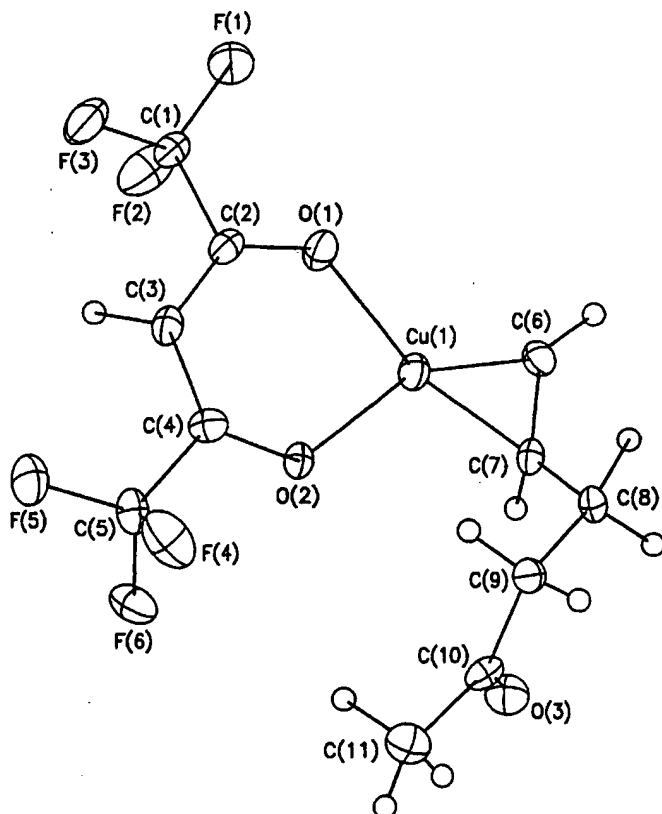
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(54) Title: COPPER SOURCE REAGENT COMPOSITIONS, AND METHOD OF MAKING AND USING SAME FOR MICRO-ELECTRONIC DEVICE STRUCTURES



(57) Abstract: Copper precursors useful in liquid delivery CVD for forming a copper-containing material on a substrate. The disclosed copper precursors are particularly useful for metalization of interconnections in semiconductor device structures.

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**COPPER SOURCE REAGENT COMPOSITIONS, AND METHOD OF  
MAKING AND USING SAME FOR MICROELECTRONIC DEVICE  
STRUCTURES**

5

**BACKGROUND OF THE INVENTION**

**Field of the Invention**

The present invention relates to copper precursor compositions and their synthesis, and  
10 to the use of such copper precursor compositions for the fabrication of microelectronic  
device structures, e.g., in the formation of copper-based interconnects in the  
manufacture of semiconductor integrated circuits, or in otherwise metallizing or  
forming copper-containing films on a substrate by metalorganic chemical vapor  
deposition (MOCVD) utilizing such precursor compositions.

15 **Description of the Related Art**

The process of fabricating semiconductor integrated circuits generally includes the  
formation of metal interconnect lines. Such metal interconnect lines often are formed  
from multiple conductive layers. For example, a thin conductive layer (termed a  
20 "barrier layer" in this context) may be formed from a metal, a metal nitride or a metal  
silicide, with a thicker conductive layer of aluminum, copper or other metal deposited  
over the barrier layer.

Many semiconductor device manufacturers are adopting copper metallization for use in production of microelectronic chips. Copper interconnects offer chip manufacturers a number of advantages, including enhanced circuit speed, improved performance and reduced electro-migration effects. Any of the one or more metal layers (e.g., bulk layer  
5 and/or seed layer) of a semiconductor integrated circuit may be formed utilizing a copper-based film. Furthermore, low resistivity, low contact resistance, and reduced RC time delays make copper particularly desirable for use in the metallization of very large scale integration (VLSI) devices.

In order to prevent detrimental effects caused by the interaction of a copper layer with  
10 other portions of the integrated circuit, a barrier layer is typically utilized in conjunction with the copper layers. Any of a wide range of barrier materials may be utilized including materials comprising metals, metal nitrides or metal silicides. Exemplary barrier materials include titanium nitride, titanium silicide, tantalum nitride, tantalum silicide, tungsten nitride, tungsten silicide and silicon doped metal nitrides. After the  
15 formation of a barrier layer, the copper is deposited on the barrier layer. The initial copper deposition may function as an electrochemical or CVD seed layer, e.g., an adhesive, conducting seed layer, followed by electrochemical plating or CVD of copper, for instance to complete the thin-film interconnect. Alternatively, the copper deposition may be employed to fully deposit the desired amount of copper.

20 For practical applications, the copper CVD precursors for the metallization composition should remain stable at room temperature and should not decompose at the vaporization temperature (e.g., the temperature required to efficiently vaporize the precursor). Concurrently, however, the precursor must decompose at elevated temperature to form high-purity Cu films on the heated substrate surface. The satisfaction of these

parameters requires a delicate balance because the difference between the vaporization temperature and the film growth temperature is typically quite small ( $\sim 100^\circ\text{C}$ ).

A suitable thermal stability can be realized by using bi-dentate neutral Lewis base ligands such as an ene-one. In this manner, the combination of the two coordination  
5 sites can be "fine-tuned." Further, chelating complexes usually exhibit better stability than monodentate complexes.

Chemical vapor deposition (CVD) of copper provides uniform coverage for the metallization. Liquid CVD precursors enable direct delivery or liquid injection of the precursors into a CVD vaporizer unit. The accurate and precise delivery rate can be  
10 obtained through volumetric metering to achieve reproducible CVD metallization during VLSI device manufacturing.

Currently only a few liquid copper precursors are commercially available. These include (hfac)Cu(MHY), (hfac)Cu(3-hexyne), (hfac)Cu(DMCOD) and (hfac)Cu(VTMS), wherein hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato, MHY = 2-  
15 methyl-1-hexen-3-yne, DMCOD = dimethylcyclooctadiene, and VTMS = vinyltrimethylsilane. However, concerns have arisen regarding perfluoro- $\beta$ -diketonate ligands, such as hfac, because the fluorine can react on the substrate surface forming a thin interface layer of  $\text{CuF}_2$ , leading to poor adhesion and high contact resistances of Cu films on the substrate. Copper CVD precursors with a reduction of fluorine-content  
20 or without fluorine are therefore highly desirable. The present invention provides new ( $\beta$ -diketonate)CuL precursors (wherein L is a coordinating ligand in the ( $\beta$ -diketonate)CuL complex) with reduced and/or eliminated fluorine content in the complexes having utility in CVD of Cu thin films.

Furthermore, to achieve a reproducible film growth process, liquid precursors are extremely desirable. To date, only a few (hfac)CuL complexes are liquids that satisfy the requirements for CVD precursors. An organic solution prepared from a solid precursor provides a significant opportunity to increase the precursor availability for various purposes. However, it is well known that the solutions of (hfac)CuL complexes display poor stability. For example, a 50% ether solution of (hfac)Cu(MHY) decomposes in a few days at room temperature while the neat precursor is stable for at least 6 months. Therefore, there is a clear need to continuously develop reliable liquid source materials (neat or in a thermally stable chemical solution) for the CVD of Cu thin films. The present invention provides new stable (hfac)CuL precursors compositions and solutions.

As previously noted, the use of various copper precursors in CVD reactors to create copper interconnects in semiconductor integrated circuits, for example, is well known. U.S. Patents 5,085,731; 5,098,516; 5,144,049; and 5,322,712 provide examples; and the references cited in these patents provide additional examples of such precursors. New and useful compositions and processes for the production of copper that improve upon, or provide alternatives to, these known compositions are highly desirable.

Copper CVD processes that are suitable for the large-scale manufacture of integrated circuits are extremely valuable to the electronics industry. Towards these ends, Cu CVD is generally used for two purposes: (1) deposition of a conductive thin-film layer as a plating base ("seed") for electroplating processes; and (2) full-fill deposition of copper interconnects, features and multi-level structures.

There is, therefore, a need in the art for new and improved copper precursors for metallization in the manufacture of integrated circuits and other microelectronic device

structures, using techniques such as CVD, plasma-assisted CVD, etc. Further, improved vaporization can lead to greatly improved deposition processes.

It is accordingly an object of the present invention to provide new copper precursors and formulations.

- 5 It is another object of the invention to provide methods of forming copper in the manufacturing of integrated circuits and other microelectronic device structures.

It is a further object of the invention to provide metallization technology for forming interconnects and other integrated device structures that overcome the shortcomings and limitations of the prior art, namely robust manufacturing.

- 10 It is another object of the invention to provide a method of metallizing or forming copper-containing thin films on a substrate by metalorganic chemical vapor deposition (MOCVD) utilizing such novel copper precursors and solution compositions.

Other objects and advantages of the present invention will be more fully apparent from the ensuing disclosure and appended claims.

15

### **SUMMARY OF THE INVENTION**

The present invention relates to copper source reagent compositions, and to methods of making, stabilizing and using the same.

- In one broad aspect, the present invention relates to novel ( $\beta$ -diketonate)CuL precursors  
20 with increased thermal stability, with reduced fluorine content (relative to various corresponding commercial copper source reagents) and having utility for chemical vapor deposition (CVD) of copper thin films (i.e., copper deposited at a thickness of

less than about 1000  $\mu\text{m}$ ), as well as to methods for making and using such precursors and compositions.

In another aspect, the present invention relates to methods of synthesizing ( $\beta$ -diketonate) $\text{CuL}$  complexes, comprised of reacting  $\text{Cu}_2\text{O}$  with corresponding ( $\beta$ -diketonate) $\text{H}$  in the presence of the desired Lewis base ligands,  $\text{L}$ , yielding complexes  
5 with increased thermal stability and/or reduced fluorine content as compared to the existing commercial copper MOCVD precursors.

In another embodiment the present invention relates to partially fluorinated or non-fluorinated  $\beta$ -diketonates, such as tfac and tfdac and thd.

10 In a specific aspect, the present invention provides a CVD process that uses the aforementioned copper precursors, that may alternatively be in the form of neat liquid, as well as solution compositions of solid and liquid precursors of such type, for copper metallization or for forming copper seed layers, e.g., by direct liquid injection and vaporization. Vaporization may be effected by heating, by acoustics, by ultrasound or  
15 by nebulization.

The present invention also relates to novel stable ( $\text{hfac}$ ) $\text{CuL}$  precursors and to stable solutions for chemical vapor deposition of copper-containing thin films.

Another aspect of the invention relates to a method of forming a plating base "seed" layer on a substrate for subsequent electroplating, comprising deposition on the  
20 substrate of a layer of copper-containing material by liquid delivery CVD using a liquid-phase copper precursor, that is thermally stable at liquid delivery process temperatures, to form the layer of copper-containing material as the electrically conductive plating base seed layer.



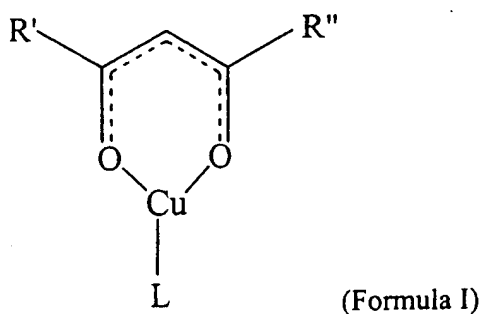
A still further aspect of the invention relates to a microelectronic device structure comprising a substrate having a chemical vapor deposited copper plating base seed layer on the substrate, wherein the copper plating base seed layer has been formed using a liquid-phase copper precursor that is thermally stable at liquid delivery  
5 temperatures (at which the precursor liquid is vaporized to form a corresponding precursor vapor), but which is readily decomposable at chemical vapor deposition condition temperatures, to yield a copper-containing film on the substrate with which the precursor vapor is contacted.

Another aspect of the invention relates to a method of full-fill copper metallization of a  
10 microelectronic device structure, comprising liquid delivery chemical vapor deposition of copper metallization on the microelectronic device structure.

In a further aspect, the invention relates to methods of synthesizing ( $\beta$ -diketonate)CuL complexes by reacting  $\text{Cu}_2\text{O}$  with the corresponding ( $\beta$ -diketonate)H in the presence of Lewis base ligand(s), L, yielding complexes having increased thermal stability and/or  
15 reduced fluorine content as compared to the existing commercial copper precursors.

In a specific compositional aspect, the invention relates to a ( $\beta$ -diketonate)CuL complex, selected from the group consisting of:

Precursors of Formula I

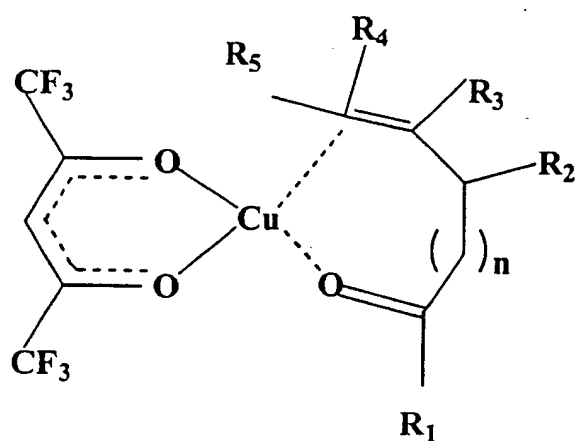


wherein

R' and R'' are the same or different and are independently selected from the group consisting of C<sub>1</sub> – C<sub>8</sub> acyclic alkyl, aryl, fluoroaryl, C<sub>1</sub> – C<sub>8</sub> fluoroalkyl, C<sub>3</sub>-C<sub>6</sub> cycloalkyl, and C<sub>3</sub>-C<sub>6</sub> fluorocycloalkyl; and

- 5 L is a neutral Lewis base ligand, selected from the group consisting of (i) alkenes, (ii) alkynes, (iii) silicon, and (iv) sulfur, oxygen and/or nitrogen-containing organic ligands;

(b) precursors of Formula II:



(Formula II)

- 10 wherein

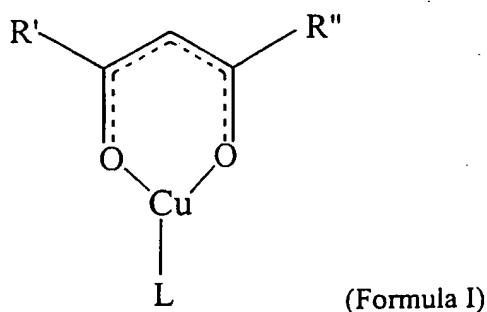
R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> may be the same or different and are independently selected from the group consisting of H, aryl, fluoroaryl, C<sub>1</sub> – C<sub>8</sub> acyclic alkyl, C<sub>1</sub> – C<sub>8</sub> fluoroalkyl, or C<sub>3</sub>-C<sub>6</sub> cycloalkyl, and

n is 0, 1, 2, or 3. The bonding mode can be intermolecular or intramolecular.

Another aspect of the invention relates to a method of forming a copper-containing material on a substrate, comprising vaporizing a copper precursor composition to form a precursor vapor, and contacting the precursor vapor with a substrate to form the copper-containing material thereon, wherein the copper precursor composition includes

5 at least one precursor selected from the group consisting of:

(a) precursors of Formula I



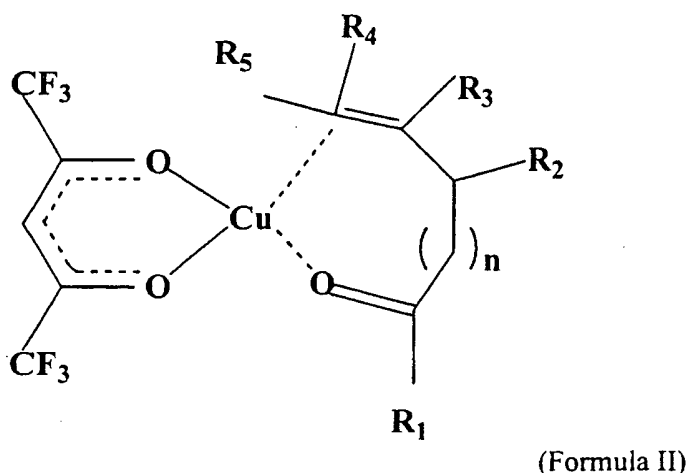
wherein

10 R' and R'' are the same or different and are independently selected from the group consisting of C<sub>1</sub> – C<sub>8</sub> acyclic alkyl, aryl, fluoroaryl, C<sub>1</sub> – C<sub>8</sub> fluoroalkyl, C<sub>3</sub>-C<sub>6</sub> cycloalkyl, and C<sub>3</sub>-C<sub>6</sub> fluorocycloalkyl; and

L is a neutral Lewis base ligand, selected from the group consisting of (i) alkenes, (dienes), (ii) alkynes, (iii) silicon, and (iv) sulfur, oxygen and/or nitrogen-containing

15 organic ligands;

(b) precursors of Formula II:



wherein

$R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  may be the same or different and are independently selected from the group consisting of H, aryl, fluoroaryl,  $C_1 - C_8$  acyclic alkyl,  $C_1 - C_8$  fluoroalkyl, or

5  $C_3 - C_6$  cycloalkyl, and

$n$  is 0, 1, 2, or 3.

Other aspects and features of the invention will be more fully apparent from the ensuing disclosure and appended claims.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

10

Figure 1 is a thermal analysis graph for (hfac) Cu(5-hexen-2-one).

Figure 2 is an X-ray single crystal diffraction analysis of (hfac)Cu(5-hexen-2-one).

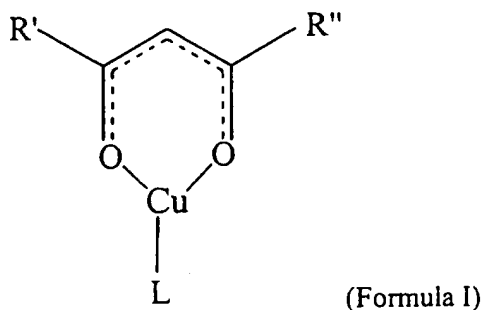
Figure 3 is an X-ray single crystal diffraction analysis of two (hfac)Cu(5-hexen-2-one) monomers displaying near neighbor interaction.

**DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED  
EMBODIMENTS THEREOF**

The present invention provides new copper precursors for use in the deposition of  
5 copper.

In one aspect, the present invention provides novel ( $\beta$ -diketonate)CuL precursors with reduced or eliminated fluorine content, in relation to commercially employed corresponding copper precursors of the prior art. The precursors of the present invention have utility in the chemical vapor deposition formation of copper thin films.

10 One class of such ( $\beta$ -diketonate precursors has the formula:



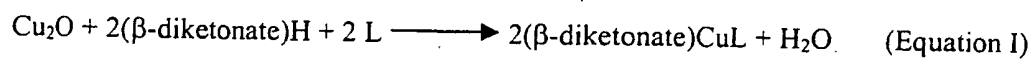
wherein

R' and R'' are the same or different and are independently selected from the group consisting of C<sub>1</sub> – C<sub>8</sub> acyclic alkyl, aryl, fluoroaryl, C<sub>1</sub> – C<sub>8</sub> fluoroalkyl,  
15 C<sub>3</sub>-C<sub>6</sub> cycloalkyl, and C<sub>3</sub>-C<sub>6</sub> fluorocycloalkyl; and

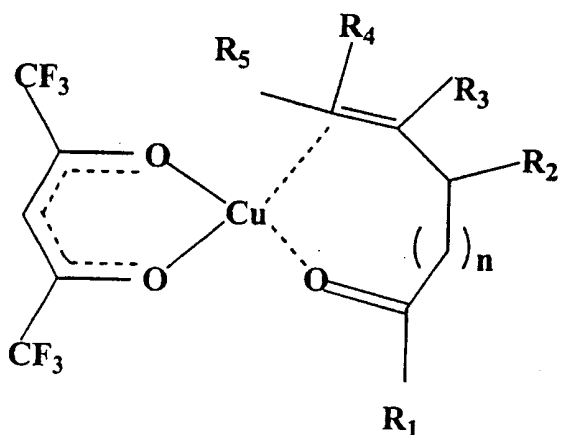
L is a neutral Lewis base ligand, selected from the group consisting of (i) alkenes, (ii) alkynes, (iii) silicon, and (iv) sulfur, oxygen and/or nitrogen - containing organic ligands.

In a preferred aspect, the complexes of Formula I have from 0 to 6 fluorine atoms, with decreasing numbers of fluorine atoms being progressively more preferred. In a most preferred aspect, the complexes have no fluorine atoms.

The complexes of the form  $(\beta\text{-diketonate})\text{CuL}$  are readily synthesized by reacting  $\text{Cu}_2\text{O}$  with the corresponding  $(\beta\text{-diketonate})\text{H}$  in the presence of the Lewis base ligand, L, as illustrated in the Equation I:



Another class of copper precursor reagents of the present invention, having improved stability, has the formula (hfac)CuL, i.e.,



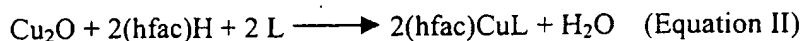
(Formula II)

wherein

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> may be the same or different and are independently selected from the group consisting of H, aryl, fluoroaryl, C<sub>1</sub> – C<sub>8</sub> acyclic alkyl, C<sub>1</sub> – C<sub>8</sub> fluoroalkyl, or C<sub>3</sub>-C<sub>6</sub> cycloalkyl, and

15  $n$  is 0, 1, 2, or 3.

The complexes of Formula II are synthesized by reacting  $\text{Cu}_2\text{O}$  and  $\text{hfacH}$  in the presence of a Lewis base ligand as illustrated in the following equation:



The complexes of Formulas I and II may be provided as liquids (which may be used  
5 directly) or solids (which may be used in a solution composition formed by dissolving the solid precursor(s) in a suitable solvent medium that provides for long-term stability).

In one embodiment, the present invention provides liquid compositions comprising complexes of Formula I and/or II, wherein L is a neutral Lewis base ligand, such as,  
10 ene-one, yne-one, yne-yne, ene-amine and ene-imine, and the complex is either a liquid phase material, or else a solid that has been dissolved in a suitable stabilizing solvent medium. Preferably, the selected solvent has weak donor-capability to stabilize the composition. The solvent for example may be an alkene, such as 1-hexene or cyclohexene. The percentage of the precursor in solution may range from 1 to 99.99%  
15 by weight, based on the total weight of the solution.

In another embodiment, the present invention provides solvent compositions comprising complexes of Formulas I and/or II, wherein the solvent may for example be selected from hydrocarbons, such as pentane, hexane, heptane, octane etc., or ethers, such as diethyl ether or tetrahydrofuran (THF), or aryls, such as toluene in combination  
20 with alkenes or/and alkynes for enhanced stabilization of the precursor composition. The precursors employed in the solutions may initially be solids, e.g., thermally stable solids that are further stabilized in the solution. The percentage of the precursor in the solution may range from 0.1 to 99.99% by weight, based on the total weight of the solution.

In a specific embodiment, the present invention provides a CVD process that uses one or more of the precursor materials of Formulas I and/or II, e.g., as neat liquid precursors or as a stabilized solution composition, for copper metallization or for the formation of copper seed layers, e.g., via liquid injection or direct vaporization.

- 5 In connection with the ensuing discussion, the disclosures of the following United States patents and patent applications are hereby incorporated herein by reference in their entireties:

United States Patent Application No. 08/835,768 filed April 8, 1997 in the names of Thomas H. Baum, et al.;

- 10 United States Patent Application No. 08/484,654 filed 7 June 1995 in the names of Robin A. Gardiner et al.;

United States Patent Application No. 08/414,504 filed 31 March 1995 in the names of Robin A. Gardiner et al.;

- 15 United States Application No. 08/280,143 filed July 25, 1994, in the names of Peter S. Kirlin, et al.;

United States Patent Application No. 07/927,134, filed August 7, 1992 in the same names;

United States Patent Application No. 07/807,807, filed December 13, 1991 in the names of Peter S. Kirlin, et al., now issued as United States Patent No. 5,204,314;

- 20 United States Application No. 08/181,800 filed January 15, 1994 in the names of Peter S. Kirlin, et al., and issued as United States Patent 5,453,494;



United States Application No. 07/918,141 filed July 22, 1992 in the names of Peter S. Kirlin, et al., and issued as United States Patent 5,280,012;

United States Application No. 07/615,303 filed November 19, 1990;

United States Application No. 07/581,631 filed September 12, 1990 in the names of  
5 Peter S. Kirlin, et al., and issued as U.S. Patent 5,225,561; and

United States Patent Application No. 07/549,389 filed July 6, 1990 in the names of Peter S. Kirlin, et al.

In general, the copper precursor compositions of the invention may be formulated to comprise, consist of, or consist essentially of any appropriate components herein  
10 disclosed, and such copper precursor compositions of the invention may additionally, or alternatively, be formulated to be devoid, or substantially free, of any components taught to be necessary in prior art formulations that are not necessary to the achievement of the objects and purposes of the invention hereunder.

The compositions of the present invention are useful in a number of applications. For  
15 example, the compositions may be used in the formation of copper interconnect lines in a semiconductor integrated circuit. To form such integrated circuits, a semiconductor substrate may have a number of dielectric and conductive layers formed on and/or within the substrate.

As used herein, the semiconductor substrate may include a bare substrate or a substrate  
20 having any number of layers formed thereon.

A copper-containing layer may typically be formed on the semiconductor substrate for use in a first, second, third, or subsequent metallization layer comprising a multi-level

device. Such copper layers are typically used in circuit locations requiring low resistivity and/or high speed circuit paths. As mentioned hereinabove, before a copper layer is formed upon a semiconductor substrate, a barrier layer may be formed on the substrate, with the barrier layer subsequently being overcoated with the copper layer or  
5 a copper "seed" layer.

The copper precursor compositions of the invention may be deposited on a wafer or other substrate by use of a CVD system. Metalorganic CVD (MOCVD) systems may be utilized for such purposes, such systems being well known in the semiconductor fabrication art. Preferred MOCVD systems include low-pressure CVD systems.

10 The compositions of the present invention are not limited in respect of their use with the aforementioned low-pressure CVD deposition tools, however, and other CVD tools, for example PECVD tools, or other deposition tools, may be utilized.

The compositions of the present invention may be delivered to the CVD reactor in a variety of ways. For example, a liquid delivery system may be utilized. Such systems  
15 generally include the use of liquid MFCs (mass flow controllers). An exemplary liquid delivery system that may be used is the ADCS Sparta 150 Liquid Delivery System (commercially available from ATMI, Inc., Danbury, CT).

Liquid delivery systems generally meter a desired flow rate of the precursor composition in liquid form to the CVD process tool. At the process tool chamber, or  
20 upstream thereof, the liquid may be vaporized through use of a vaporizer. Such vaporizers may utilize thermal heating, acoustics, ultrasound and high flow nebulizers. Further descriptions of liquid delivery systems are contained in U.S. Patent Nos. 5,204,314; 5,362,328; 5,536,323; and 5,711,816, the disclosures of which are hereby expressly incorporated herein by reference in their entireties.

In the practice of the present invention utilizing liquid delivery, the copper precursor species, if of solid form at ambient conditions, may be dissolved or suspended in a compatible solvent medium as more fully described in U.S. Patent No. 5,820,664 issued October 13, 1998 for "Precursor Compositions For Chemical Vapor Deposition,  
5 And Ligand Exchange Resistant Metal-Organic Precursor Solutions Comprising Same," the disclosure of which is hereby incorporated herein in its entirety by reference.

The precursors of the present invention may be deposited using any chemical vapor deposition system known in the art. A preferred liquid delivery MOCVD System is  
10 described in U.S. Patent 5,204,314, issued April 20, 1993, for "Method for Delivering an Involatile Reagent in Vapor Form to a CVD Reactor," the disclosure of which is hereby incorporated herein in its entirety by reference.

The use of the compositions disclosed herein is not limited to liquid delivery systems, and any method which adequately delivers the composition to the process tool is  
15 satisfactory. Thus, for example, bubbler-based delivery systems may be utilized, but are not preferred. In such systems, an inert carrier gas is bubbled through the precursor composition (typically in liquid form above its melting point). The resulting gas, which is wholly or partially saturated with the vapor of the composition, is provided to the CVD tool.

20 A wide variety of CVD process conditions may be utilized for chemical vapor deposition employing the compositions of the present invention. Typical liquid delivery MOCVD process conditions may include substrate temperature ranges of 160-300°C, with about 170°C to about 250°C being more typical; vaporizer temperature ranges may be from about 50°C to about 150°C, with about 60°C to about 100°C being

more typical; pressure ranges are generally from about 0.05 to about 20 Torr (and most preferably from about 0.1 to about 5 Torr), with a range of about 0.2 to about 0.5 Torr being more typical; and inert gas flows of helium or argon of from about 25 - 750 sccm (and most preferably from about 50 to about 200 sccm), at a temperature approximately  
5 the same as the vaporizer. In some cases, a co-reactant may be introduced (i.e., water, alcohol or hydrogen forming gas) to facilitate the film growth process.

The following synthesis examples, including synthesis of new ( $\beta$ -diketonate)CuL complexes, wherein  $\beta$ -diketonate = 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionate, (tfdac) 1,1,1-trifluoro-2,4-hexanedionate, (tfac) or 1,1,1,5,5,5-hexafluoro-2,4-  
10 hexanedionate, (hfac); L = dimethyldivinylsilane (DMDVS) or 2-methyl-1-hexen-3-yne (MHY), are representative of specific aspects of the invention and are not intended to limit the scope of the invention or claims hereto. Each of the following general reactions was carried out under a steady flow of nitrogen.

### EXAMPLE I

#### 15 [(tfdac)Cu]<sub>2</sub>(DMDVS)

A Schlenk flask was charged with 3 g of copper (I) oxide and 3 g of dimethyldivinylsilane (26.7 mmol, 1.05 equivalent on the basis of tfdacH) with 15 mL anhydrous methylene chloride. 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione or (tfdac)H (5.0 g, 25 mmol) in 5 mL CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to the magnetically  
20 stirred suspension at about 0 °C. After the addition, the suspension was stirred for an additional 12 hours at room temperature. The mixture was then filtered through an Al<sub>2</sub>O<sub>3</sub> column, and a light yellow filtrate was collected. Removal of volatiles from the filtrate gave 6.1 g (~ 85 %) yellow liquid. The yellow liquid was characterized by solution NMR. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>),  $\delta$ (ppm) 6.14 (s, 1H, CH of tfdac), 4.25-4.55 (m 3H,

$\text{CH}=\text{CH}_2$ ), 1.03 (s, 9H,  $\text{CH}_3$  of t-Bu), 0.17 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ),  $\delta(\text{ppm})$ , 207.8 (s,  $\text{CH}_3-\text{C}(\text{O})-$ ), 172.2 (q,  $\text{CF}_3-\text{C}(\text{O})-$ ), 120.4 (q,  $\text{CF}_3$ ), 102.2 (s,  $\text{CH}=\text{CH}_2$ ), 96.7 (s,  $\text{CH}=\text{CH}_2$ ), 91.1 (s,  $\text{CH}$ ), 42.9 (s,  $-\text{C}(\text{CH}_3)_3$ ), 28.2 (s,  $-\text{C}(\text{CH}_3)_3$ ), -2.1 (s,  $\text{Si}-(\text{CH}_3)_2$ ).

### EXAMPLE II

#### 5 (tfdac)Cu(MHY)

The compound was synthesized as described above, resulting in a white crystalline solid.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ),  $\delta(\text{ppm})$  6.09 (s, 1H,  $\text{CH}$  of tfdac), 5.65 (m, 1H,  $\text{H}_a\text{CH}_b=\text{C}$  of MHY), 5.09 (m, 1H,  $\text{H}_a\text{CH}_b=\text{C}$  of MHY), 2.24 (q, 2H,  $\text{CH}_2\text{CH}_3$ ), 1.82 (m, 3H,  $\text{CH}_3$  of MHY), 1.02 (s, 9H,  $\text{CH}_3$  of t-Bu), 1.0 (t, 3H,  $\text{CH}_2\text{CH}_3$  of MHY).

### 10 EXAMPLE III

#### (tfac)Cu<sub>2</sub>(DMDVS)

The compound was synthesized as described above, resulting in a white crystalline solid.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ): 0.17 (s,  $\text{CH}_3$  of DMDV), 1.68 (s,  $\text{CH}_3$  of tfac), 4.3-4.95 (m,  $\text{SiCH}=\text{CH}_2$  of DMDVS), 5.7 (s,  $\text{CH}$  of tfac);  $^{13}\text{C}$ -NMR, -2.67 (s), 28.73 (s), 95.35 (s),

15 103.9, (s) 109.3 (s), 119.8 (q), 171.1 (q).

### EXAMPLE IV

#### (hfac)Cu<sub>2</sub>(DMDVS)

The compound was synthesized as described above, resulting in a white light yellow liquid. NMR ( $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ , 0.04 (s, 6H,  $\text{CH}_3$ ), 4.3-4.9 (m, 6H,  $\text{CH}=\text{CH}_2$  of DMDVS), 6.17 (s, 1H,  $\text{CH}$  of hfac),  $^{13}\text{C}$ , -3.05 (s), 90.2 (s), 105.8 (s), 111.3 (s) 118.3 (q), 178.3 (q). MPLE I

**EXAMPLE V****Synthesis and Characterization of (hfac)Cu(5-hexen-2-one)**

A Schlenk flask was charged with 4.0 g of copper (I) oxide and 2.6 g (27 mmol, 1.1 equivalent on the basis of hfacH) of 5-hexen-2-one with 10 mL anhydrous methylene chloride. 1,1,1,5,5,5-hexafluoroacetylacetone (hfacH) (5.0 g, 24 mmol) in 5 mL CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to the magnetically stirred suspension at about -10 °C. After the addition of hfacH, the suspension was stirred for additional 24 hours at room temperature. The mixture was then filtered through a neutral Al<sub>2</sub>O<sub>3</sub> column and a light yellow filtrate was collected. Removal of volatiles of the filtrate gave 6.2 g (~ 70 %) yellow solid. The yellow solid was characterized by solution <sup>1</sup>H NMR. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>), δ(ppm) 6.22 (s, 1H, CH of hfac), 4.42 (m = t x d x d, 1H, CH=CH<sub>2</sub>), 3.56 - 3.66 (m, 2H, CH=CH<sub>2</sub>), 1.78 (t, 2H, CH<sub>2</sub>-CH=CH<sub>2</sub>), 1.60 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 1.56 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>), δ(ppm), 208 (s, CH<sub>3</sub>-C(O)-), 178.2 (q, CF<sub>3</sub>-C(O)-), 118.6 (q, CF<sub>3</sub>), 104.3 (s, =CH-C(O)), 89.6 (s, CH<sub>2</sub> of hfac), 80.3 (s, =CH<sub>2</sub>), 40.6 (s, -CH<sub>2</sub>-C(O)), 29.2 (s, -CH<sub>2</sub>-CH=) and 27.4 (s, -C(O)-CH<sub>3</sub>).

**EXAMPLE VI**

X

**Preparation of stable liquid composition of (hfac)Cu(5-hexen-2-one)**

One gram of (hfac)Cu(5-hexen-2-one) was dissolved in one gram of 1-hexene (approximately 1.8 M). A clear yellow solution was obtained. The solution remained at room temperature for at least 10 weeks without decomposition, indicating that the thermal stability of the solution was very good. Referring now to the drawings, Figure 1 is a plot of precursor transport (TGA) and melting point (DSC) curves for the (hfac)Cu(5-hexen-2-one) complex of the present invention, having a melting point of

about 75 °C. This material exhibits superior stability and transport in the temperature range of between about 75 °C. and 175 °C.

Figure 2 is an x-ray single crystal diffraction analysis of the (hfac)Cu(5-hexen-2-one) complex of the present invention. The single crystal x-ray diffraction structural determination conclusively shows the (hfac)Cu(5-hexen-2-one) complex of the present invention to be of mononuclear form.

Figure 3 further evidences the superior stability of the material in the solid phase to be due in part to interaction between the ketone group from the L group of one molecule of the complex with the Cu atom of a second molecule of the complex. The interaction between the two atoms imparts additional stability to the complex in the solid phase.

Other embodiments of this invention will be readily apparent to those of ordinary skill in the art, based on the disclosure herein. For example, the addition of stabilizers, water, hfac hydrate or other co-reactants may be advantageously employed.

The liquid delivery approach achieves reproducible film growth and uniform deposition rates. A combined liquid delivery and flash vaporization process may be employed, as for example utilizing an LDS300 liquid delivery and vaporizer unit (commercially available from ATMI, Inc., Danbury, CT), to enable low volatility materials to be volumetrically delivered, leading to reproducible transport and deposition without thermal decomposition of the precursor. Both of these considerations are essential to providing a commercially acceptable copper MOCVD process.

The deposition of copper thin films with useful electrical properties (low resistivity) and good adhesion to the barrier layer (e.g., formed of TiN or TaN), is also accommodated by the process and precursors of the present invention. The

conformality of the deposited film is practically achievable only through CVD techniques, which thereby provide a pathway to the achievement of "full-fill" copper metallization. The liquid delivery approach, including "flash" vaporization and the use of copper precursor chemistry as herein disclosed, enables next-generation device geometries and dimensions to be attained, e.g., a conformal vertical interconnect of 0.13 micron linewidth with 4-8:1 aspect ratio. The conformal deposition of interconnects at these critical dimensions cannot be realized by currently available physical deposition methods. Thus, the approach of the present invention affords a viable pathway to future generation devices, and embodies a substantial advance in the art. Further, improved adhesion and low contact resistances are other improvements over the prior art.

The copper precursors of the invention may be utilized in various CVD processes for copper metallization or the formation of a copper seed layer via either liquid injection or direct vaporization.

The instant invention also enables liquid delivery CVD of copper electroplating base "seed" layers. The use of thermally stable copper precursors, such as the precursors of Formula II of the present invention, provides a distinct advantage for copper CVD, especially for the deposition of the plating base layer. The enhanced thermal stability of this precursor eliminates the need for additives to stabilize the compound. Further, the thermal stability of the precursor allows liquid delivery techniques to be used to achieve reproducible film growth and uniform deposition rates. The combined liquid delivery and enhanced thermal stability allows low volatility materials to be volumetrically delivered, leading to reproducible transport and deposition.



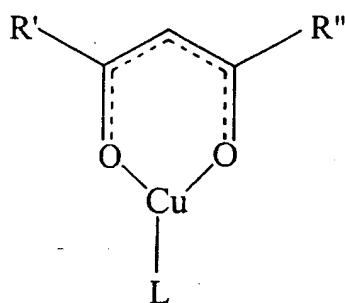
This approach thus produces a conformal, thin-film with good electrical properties and high adhesion to the barrier layer, thereby enabling electroplating technologies to be extended to next-generation device geometries and dimensions, e.g., a conformal plating base with 0.13  $\mu\text{m}$  linewidths and 4-8:1 aspect ratio vias.

- 5 While the invention has been described herein with reference to specific features and illustrative embodiments, it will be recognized that the utility of the invention is not thus limited, but rather extends to and encompasses other features, modifications and alternative embodiments, as will readily suggest themselves to those of ordinary skill in the art based on the disclosure and illustrative teachings herein. The claims that follow
- 10 are therefore to be construed and interpreted, as including all such features, modifications and alternative embodiments within their spirit and scope.

THE CLAIMSWhat is claimed is:

1. A copper source reagent composition, comprising at least one copper precursor  
 5 selected from the group consisting of:

(a) copper complexes of the formula:



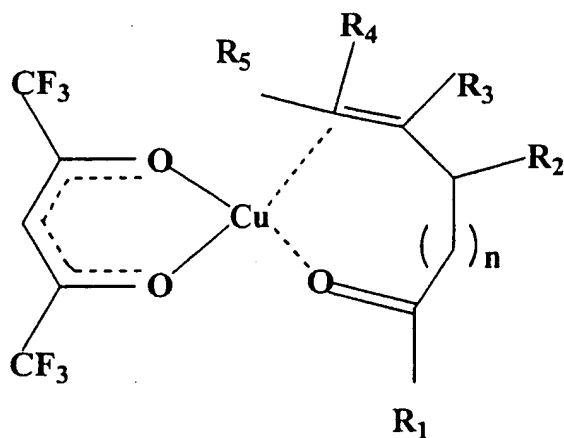
(Formula I)

wherein

- R', R'', are the same or different and are independently selected from the group  
 10 consisting of C<sub>1</sub> – C<sub>8</sub> acyclic alkyl, aryl, fluoroaryl, C<sub>1</sub> – C<sub>8</sub> fluoroalkyl, or C<sub>3</sub>-C<sub>6</sub>  
 cycloalkyl, and C<sub>3</sub>-C<sub>6</sub> fluorocycloalkyl; and

L is a neutral Lewis base ligand, selected from the group consisting of (i) alkenes, (ii)  
 alkynes, (iii) silicon, and (iv) sulfur, oxygen and/or nitrogen-containing organic  
 ligands; and

- 15 (b) copper complexes of the formula:



Formula II)

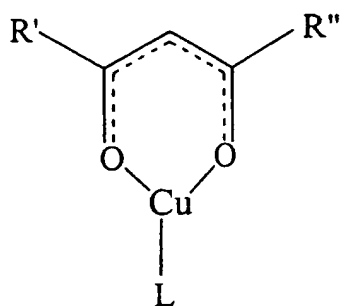
wherein

$R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  may be the same or different and are independently selected from the group consisting of H, aryl, fluoroaryl,  $C_1 - C_8$  acyclic alkyl,

5  $C_1 - C_8$  fluoroalkyl, or  $C_3 - C_6$  cycloalkyl, and

$n$  is 0, 1, 2, or 3

2. The composition according to claim 1 wherein the precursor comprises a copper complex of the formula:



(Formula I)

10

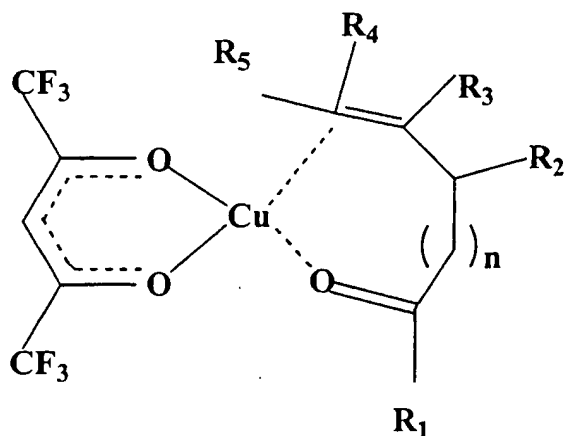
wherein

R', R'', are the same or different and are independently selected from the group consisting of C<sub>1</sub> - C<sub>8</sub> acyclic alkyl, aryl, fluoroaryl, C<sub>1</sub> - C<sub>8</sub> fluoroalkyl, or C<sub>3</sub> - C<sub>6</sub> cycloalkyl, and C<sub>3</sub> - C<sub>6</sub> fluorocycloalkyl; and

L is a neutral Lewis base ligand, selected from the group consisting of (i) alkenes, (ii) alkynes, (iii) silicon, and (iv) sulfur, oxygen and/or nitrogen -containing organic ligands.

3. The composition according to claim 1 wherein the total number of fluorine atoms is 0 to 6.
4. The composition according to claim 1 wherein the total number of fluorine atoms is 0 to 5.
5. The composition according to claim 1 wherein the total number of fluorine atoms is 0 to 4.
6. The composition according to claim 1 wherein the total number of fluorine atoms is 0 to 3.
7. The composition according to claim 1 wherein the total number of fluorine atoms is 0 to 2.
8. The composition according to claim 1 wherein the total number of fluorine atoms is 1.
9. The composition according to claim 1 wherein the total number of fluorine atoms is 0.
10. The composition according to claim 1 substantially free of fluorine.

11. The composition according to claim 1 wherein the precursor comprises a copper complex of the formula:



Formula II)

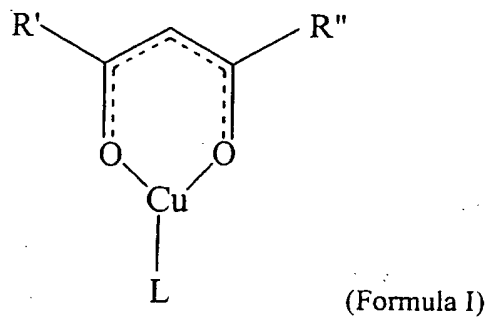
5                    wherein.

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> may be the same or different and are independently selected from the group consisting of H, aryl, fluoroaryl, C<sub>1</sub> - C<sub>8</sub> acyclic alkyl, C<sub>1</sub> - C<sub>8</sub> fluoroalkyl, or C<sub>3</sub> - C<sub>6</sub> cycloalkyl, and

$n$  is 0, 1, 2, or 3.

10 12. A method for producing of copper, said method comprising vaporizing a composition comprising a copper precursor selected from the group consisting of:

(a) copper complexes having the formula:

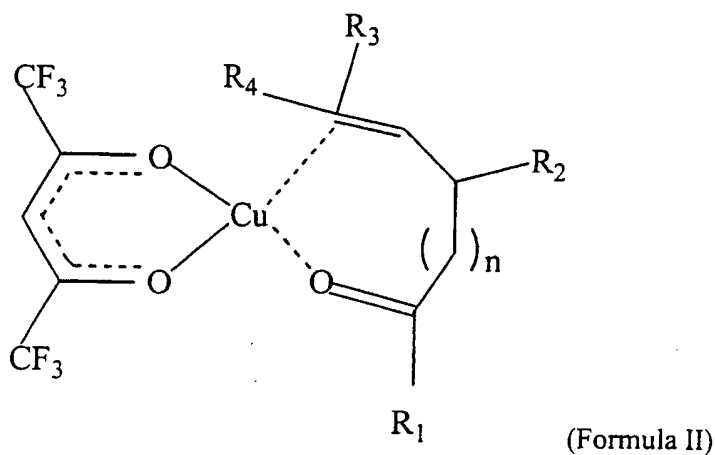


wherein

R' and R'' are the same or different and are independently selected from the group consisting of C<sub>1</sub> - C<sub>8</sub> acyclic alkyl, aryl, fluoroaryl, C<sub>1</sub> - C<sub>8</sub> fluoroalkyl, C<sub>3</sub> - C<sub>6</sub> cycloalkyl, and C<sub>3</sub> - C<sub>6</sub> fluorocycloalkyl; and

L is a neutral Lewis base ligand, selected from the group consisting of (i) alkenes, (ii) alkynes, (iii) silicon, and (iv) sulfur, oxygen and/or nitrogen - containing organic ligands; and

(b) copper complexes having the formula:



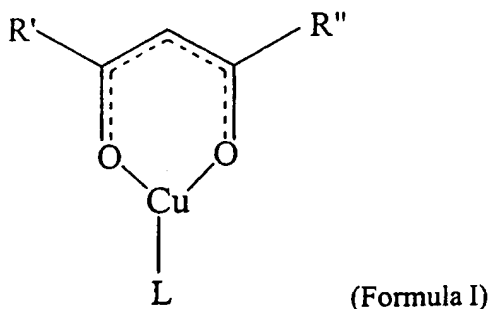
wherein

$R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and are selected from the group consisting of H, aryl, fluoroaryl,  $C_1 - C_8$  acyclic alkyl,  $C_1 - C_8$  fluoroalkyl, or  $C_3 - C_6$  cycloalkyl, and

$n$  is 0, 1, 2, or 3.

- 5 13. Copper made by the process of subjecting to CVD a composition comprising a copper precursor selected from the group consisting of:

(a) copper complexes having the formula:

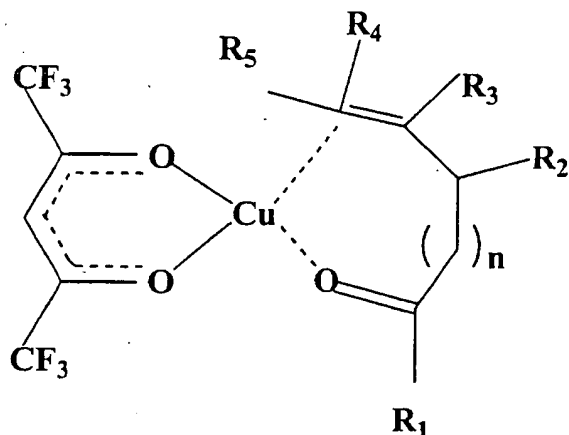


wherein

- 10  $R'$  and  $R''$  are the same or different and are independently selected from the group consisting of  $C_1 - C_8$  acyclic alkyl, aryl, fluoroaryl,  $C_1 - C_8$  fluoroalkyl,  $C_3 - C_6$  cycloalkyl, and  $C_3 - C_6$  fluorocycloalkyl; and

$L$  is a neutral Lewis base ligand, selected from the group consisting of (i) alkenes, (ii) alkynes, (iii) silicon, and (iv) sulfur, oxygen and/or nitrogen -  
15 containing organic ligands; and

(b) copper complexes having the formula:



Formula II)

wherein

$R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and are independently selected from the group consisting of H, aryl, fluoroaryl,  $C_1 - C_8$  acyclic alkyl,  $C_1 - C_8$  fluoroalkyl, or  $C_3 - C_6$  cycloalkyl, and

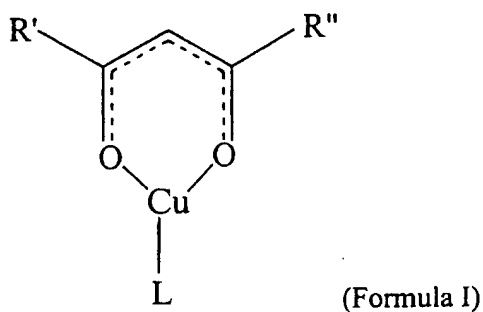
$n$  is 0, 1, 2, or 3.

14. The process of claim 12 wherein deposition of copper occurs during manufacture of an integrated circuit.
15. The process of claim 12, comprising delivering the composition to a process tool through use of a liquid delivery system.
16. An integrated circuit made using the process of claim 12.
17. The composition of claim 1 comprising at least one of said copper complexes and a solubilizing agent.



18. The composition of claim 16 wherein the solubilizing agent is an aryl, an ether, or a ketone.
19. The composition of claim 16 wherein the solubilizing agent is selected from the group consisting of pentane, hexane, heptane and octane.
- 5 20. The composition of claim 16 wherein the solubilizing agent is selected from the group consisting of diethyl ether and tetrahydrofuran.
21. The composition of claim 16 wherein the solubilizing agent is toluene.
22. A method of forming a seed layer including liquid injection or direct vaporization of a composition comprising a copper complex selected from the group consisting of:
- 10

(a) copper complexes having the formula:

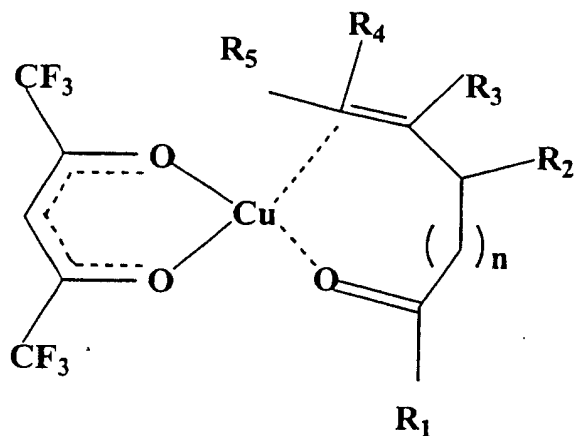


wherein

- R' and R'' are the same or different and are independently selected from the group consisting of C<sub>1</sub> - C<sub>8</sub> acyclic alkyl, aryl, fluoroaryl, C<sub>1</sub> - C<sub>8</sub> fluoroalkyl, C<sub>3</sub> - C<sub>6</sub> cycloalkyl, and C<sub>3</sub> - C<sub>6</sub> fluorocycloalkyl; and
- 15

L is a neutral Lewis base ligand, selected from the group consisting of (i) alkenes, (ii) alkynes, (iii) silicon, and (iv) sulfur, oxygen and/or nitrogen-containing organic ligands; and

1. (b) copper complexes having the formula:



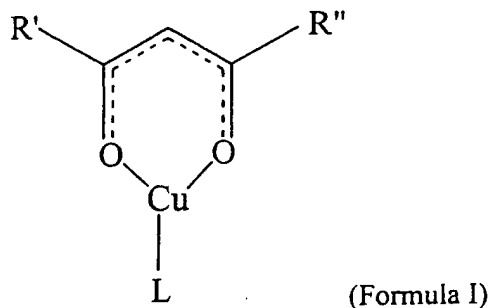
5 (Formula II)

wherein

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> may be the same or different and are selected from the group consisting of H, aryl, fluoroaryl, C<sub>1</sub> - C<sub>8</sub> acyclic alkyl, C<sub>1</sub> - C<sub>8</sub> fluoroalkyl, or C<sub>3</sub> - C<sub>6</sub> cycloalkyl, and

n is 0, 1, 2, or 3.

23. A method of making a complex having the formula:

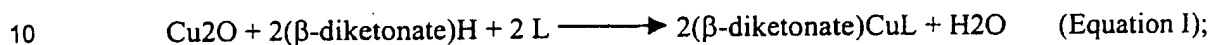


wherein

R' and R'' are the same or different and are independently selected from the group consisting of C<sub>1</sub> - C<sub>8</sub> acyclic alkyl, aryl, fluoroaryl, C<sub>1</sub> - C<sub>8</sub> fluoroalkyl, C<sub>3</sub> - C<sub>6</sub> cycloalkyl, and C<sub>3</sub>-C<sub>6</sub> fluorocycloalkyl; and

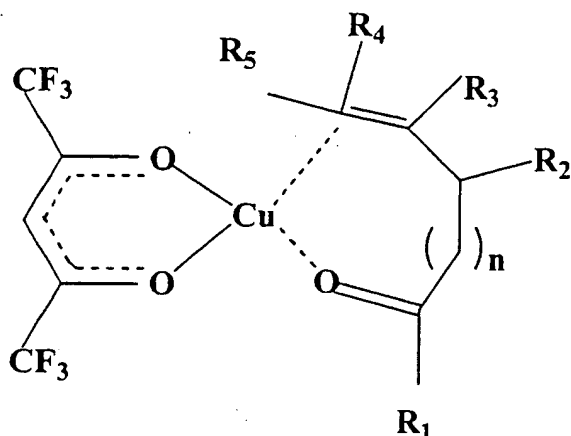
L is a neutral Lewis base ligand, selected from the group consisting of (i) alkenes, (ii) alkynes, (iii) silicon, and (iv) sulfur, oxygen and/or nitrogen-containing organic ligands;

said method comprising carrying out the reaction equation:



wherein L is as defined above.

24. A method of making a complex having the formula:



Formula II)

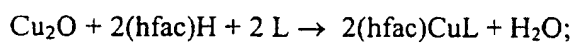
wherein

$R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and are independently selected from the group consisting of H, aryl, fluoroaryl,  $C_1 - C_8$  acyclic alkyl,  $C_1 - C_8$  fluoroalkyl, or  $C_3$

5 -  $C_6$  cycloalkyl, and

$n$  is 0, 1, 2, or 3;

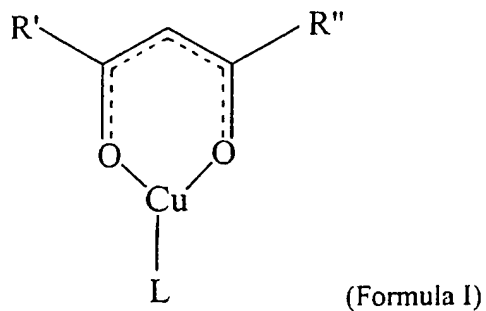
said method comprising carrying out the equation:



wherein  $L$  is as defined above.

- 10 25. A method of forming a plating base seed layer on a substrate, comprising depositing on said substrate a layer of copper-containing material by liquid delivery CVD using a liquid-phase copper precursor including at least one complex selected from the group consisting of:

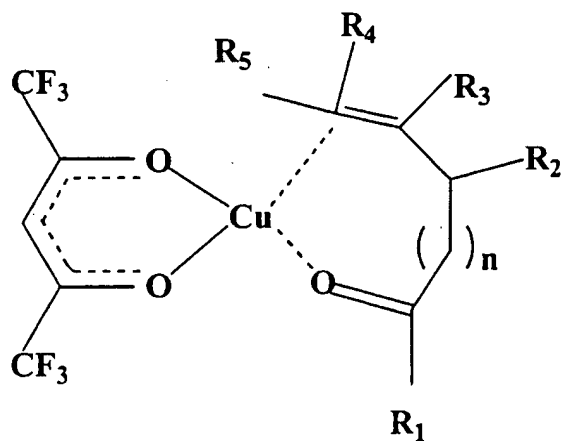
(a) copper complexes having the formula:



wherein

R' and R'' are the same or different and are independently selected from the group consisting of C<sub>1</sub> – C<sub>8</sub> acyclic alkyl, aryl, fluoroaryl, C<sub>1</sub> – C<sub>8</sub> fluoroalkyl, C<sub>3</sub> – C<sub>6</sub> cycloalkyl, and C<sub>3</sub>-C<sub>6</sub> fluorocycloalkyl; and

L is a neutral Lewis base ligand, selected from the group consisting of (i) alkenes, (ii) alkynes, (iii) silicon, and (iv) sulfur, oxygen and/or nitrogen-containing organic ligands; and



(b) copper complexes having the formula:

(Formula II)

wherein

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> may be the same or different and are selected from the group consisting of H, aryl, fluoroaryl, C<sub>1</sub> – C<sub>8</sub> open-chain alkyl, C<sub>1</sub> – C<sub>8</sub> fluoroalkyl, or C<sub>3</sub> – C<sub>6</sub> cycloalkyl, and

5 n is 0, 1, 2, or 3.

26. The method according to claim 25 utilizing a copper complex of formula I.

27. The method of claim 24 utilizing a copper complex of formula (II).

28. The method of claim 24, further comprising electroplating a conductive material on the plating base seed layer.

10 29. A microelectronic device structure comprising a substrate having a chemical vapor deposited copper plating base seed layer on the substrate, wherein the copper plating base seed layer has been formed using a liquid-phase copper precursor that is thermally stable at vaporization temperatures and is substantially free of fluorine.

15 30. The microelectronic device structure of claim 28, further comprising an electroplated metal on the copper plating base seed layer.

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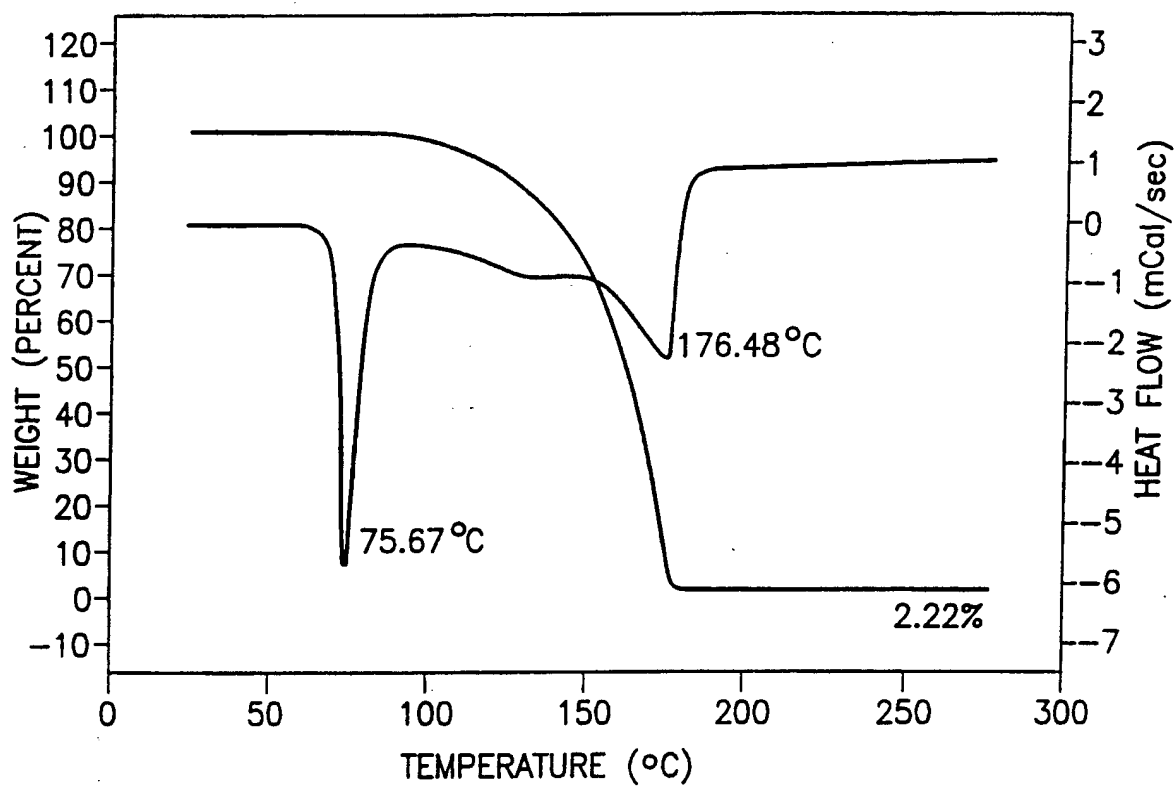


FIG. 1

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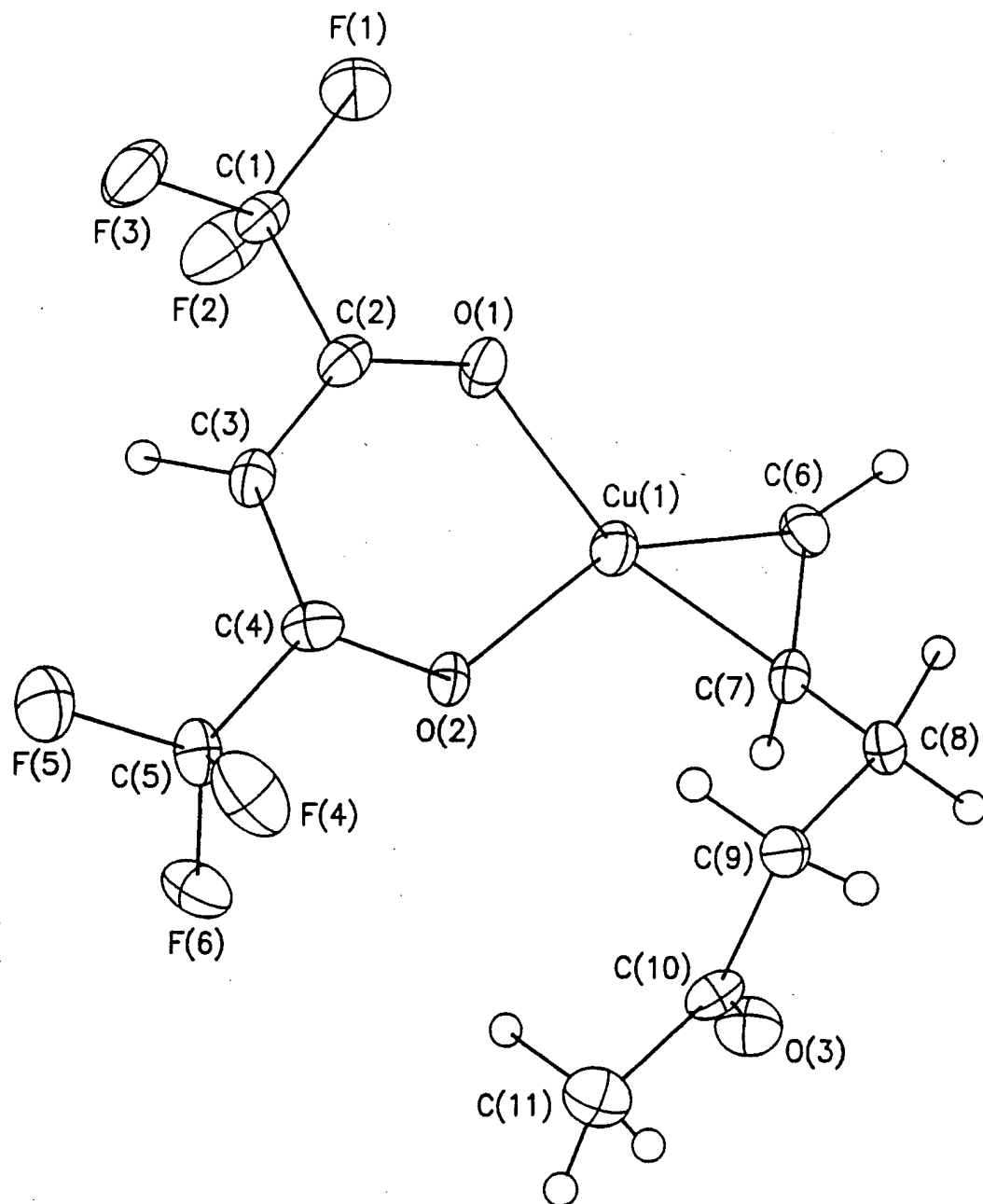


FIG.2



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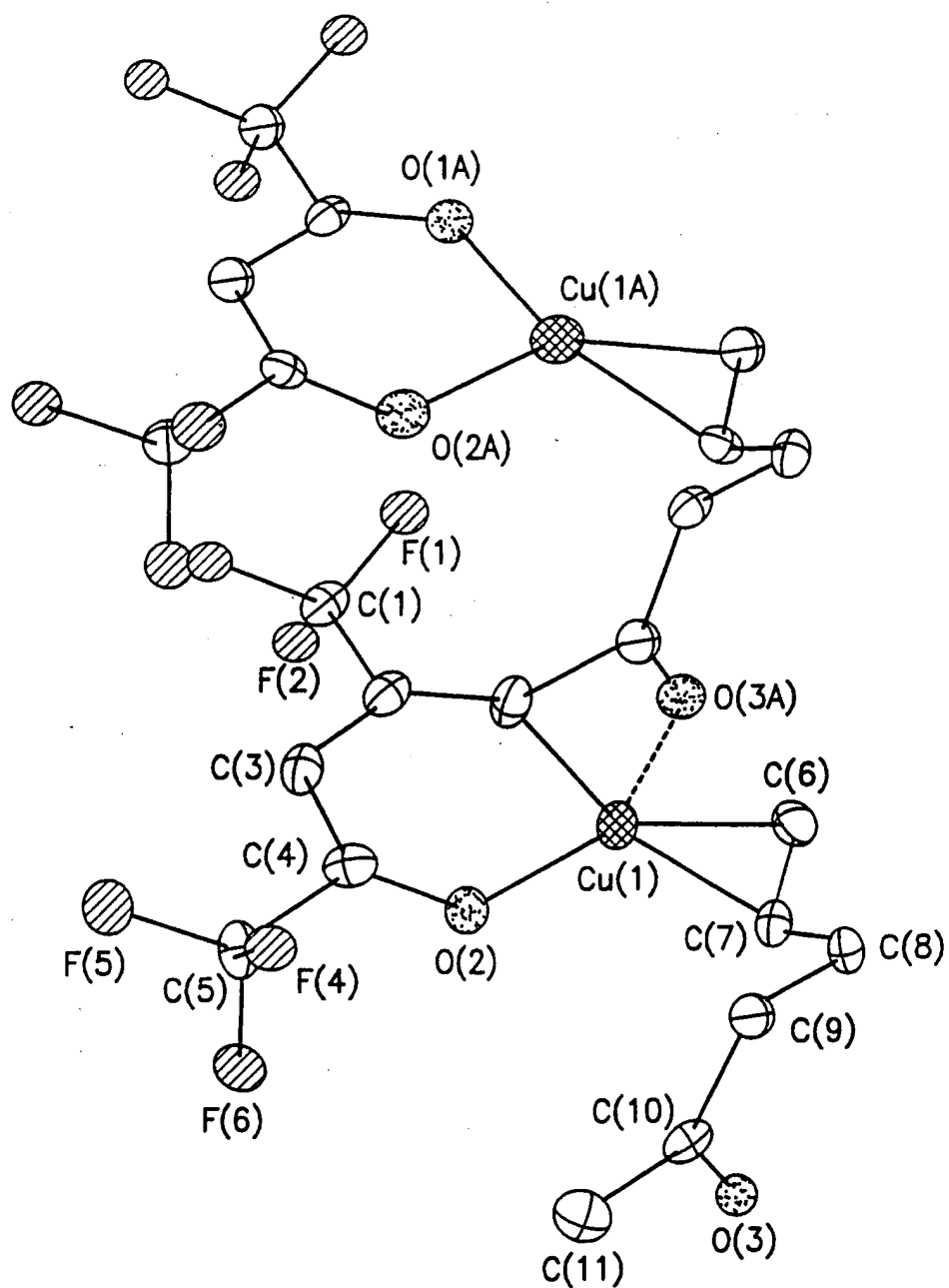


FIG.3

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/14063

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : Please See Extra Sheet.

US CL : 556/110; 427/585, 96; 106/1.25; 174/68.1; 428/674; 257/499

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 556/110, 112, 40; 427/585, 588, 252, 96; 106/1.25, 1.26; 117/104; 174/68.1, 70R; 428/674, 457; 257/499

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,358,743 A (HAMPDEN-SMITH et al) 25 October 1994, Abstract; col. 4, line 6 through col. 5, line 16; and Claims.	1-3, 12, 13 --- 14-16, 22, 25, 26, 29, 30
X --- Y	US 5,840,897 A (KIRLIN et al) 24 November 1998, Abstract; Table 1; col. 15, line 52 through col. 16, line 2; and Examples 24, 26, and 28.	1-7, 9, 10, 12, 13, 22, 25, 26 --- 14-21, 29, 30
X	US 5,817,367 A (CHUN et al) 06 October 1998, Abstract; col. 2, line 60 through col. 5, line 20.	1-3, 12-14, 16, 22, 25, 26, 29, 30

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

10 AUGUST 2000

Date of mailing of the international search report

28 AUG 2000

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/14063

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,767,301 A (SENZAKI et al) 16 June 1998, Abstract; Figures 6-8; col. 6, line 18 through col. 8, line 31; col. 8, line 48 through col. 9, line 23; col. 12, lines 17-38; col. 12, line 65 through col. 13, line 25; col. 13, line 65 through col. 14, line 10.	1-3, 12-18, 22, 23, 25, 26, 29 and 30
X	US 5,322,712 A (NORMAN et al.) 21 June 1994, col. 3, line 59 through col. 4, line 37; col. 6, line 18 through col. 7, line 39; and Claims.	1-3, 12, 13, 15, 17, 18, 20, 22, 25, 26
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Y		4-10, 14, 16, 29, 30

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/14063

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (7):

C07F 1/08; B05D 5/12; C23C 16/18; H01B 1/02; B32B 15/20; H01L 21/00

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